

The Use of Solid State C-13 NMR Spectroscopy to Study Pyridine Extracted and Extraction Residues in the Argonne Premium Coals

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INTRODUCTION

The relationship between coal structure and combustion behavior is a matter of on-going research in our laboratories. A great deal of effort has gone into obtaining data that is used for modeling studies of devolatilization behavior.¹ We have also carefully studied the process of char formation.²⁻³ Our past work has focused on trying to understand the relationship between coal/char/tar formation² as they relate to the devolatilization and char oxidation phenomena. The formation of metaplast during pyrolysis was studied by Fong and Howard⁵ in terms of extractable material obtained at different stages of the devolatilization process. We have recently turned our attention to metaplast formation in devolatilization and plan to conduct a series of experiments that will help define the formation and chemical structure of metaplast in coals of different rank.

Howard and Fong used pyridine extraction methods to quantify the amount of metaplast formed during pyrolysis of a Pittsburgh #8 coal. These experiments demonstrated that pyridine extractable material initially increased with pyrolysis temperature, passed through a maximum, and then decreased as retrogressive reactions became dominant at the higher temperatures. We have completed an initial study of the pyridine extraction of the Argonne Premium coal samples and the detailed study of the carbon skeletal structure of the extracts and the extraction residues from these coals. The ¹³C NMR data obtained from these extracts and extraction residues will be compared with the extracts and extraction residues formed at different stages of the pyrolysis process in these coals as our pyrolysis work develops.

EXPERIMENTAL

It is well known that a considerable amount of material is extracted by pyridine from bituminous coals. However, a significant part of the extract seems to form colloidal dispersions that can be disruptive to analytical techniques such as proton and carbon NMR spectroscopy. It is also known that pyridine is imbibed into the structure of coal and is very difficult to remove. This imbibed pyridine makes it difficult to quantify the structural features of coals. We adopted the technique of Buchanan⁶ in an effort to minimize the formation of colloidal dispersions. Extractions were carried out at room temperature after the manner of Buchanan's procedure with the extraction process taking as much as three days to complete. It was judged that extraction was complete at the point that the pyridine recycle solvent in the Abderhalden extraction apparatus was colorless. The samples were then washed as described by Buchanan and dried at room temperature in a vacuum to remove solvents. Proton NMR spectra were then obtained on the extract to determine the level of incorporation of pyridine into the extract material. In all cases only minor traces of pyridine were observed in the proton NMR spectra.

The carbon-13 NMR spectra of all extracts and extraction residues were obtained according to the procedure of Solum, et al.⁷ High resolution NMR data was obtained on a Varian VXR-500 spectrometer using dimethyl sulfoxide as solvent. It was noted that the solubility of the extracts varied with the coal and that solubilization was not complete for any of the coals. The NMR spectra exhibited the characteristics of high resolution with line widths that would be typical of compounds with molecular weights of several hundred daltons.

RESULTS

The amount of extract obtained from each of the 8 Argonne Premium coals is given in Table 1. The duplicate extractions were run in parallel and the reproducibility of the results appears to be quite adequate. It is noted that a mass closure of at least 94% was obtained on each sample. Figure 1 portrays the extract yield together with the fraction of total carbons that are protonated aromatic carbons in the pyridine extracts and residues. In each case this parameter is found to be higher in the extract than in the residue, indicating that the residue contains a higher fraction of substituted carbons than the extract. In Figure 2, the coordination number of the residues is higher than the extracts with the single exception of the Illinois #6 in which no distinction can be made. The number of bridges and loops in the residues and extracts are shown in Figure 3. This parameter is a measure of the cross link structure that exists between individual aromatic clusters. As one might expect, the residues exhibit a greater number of bridges than are found in the extracts. The single exception, again, is the Illinois #6 coal in which no distinction can be made between the two. In Figure 4, the average aromatic cluster size is given and in each case the size of the extract is less than that of the residue, with the single exception of Illinois #6 where no clear distinction can be made. Figure 5 portrays the number of side chains per cluster in the extracts and residues. From this data no consistent trend can be observed. Figure 6 contains the aromatic characteristics of the extracts from the Argonne coals. As expected, both the carbon and proton aromaticity of the extracts increase with rank with the single exception of the Pocahontas extract. The carbon aromaticity of the residue is also plotted for comparison purposes. Using the proton structural definitions reported by Fletcher, et al.,² it is possible to approximate the contributions 1, 2, and 3-ring aromatic species in the coal extracts. These data are also shown in Figure 6. In Figure 7, the contributions of total α -hydrogens, α -methyls, α -CH₂ groups, and γ -methyls for the pyridine extracts are given. It is interesting to note that the total α -hydrogen and α -CH₂ groups pass through a maximum, as a percent of the total hydrogen in the samples, in the high volatile bituminous coal. As expected, the contributions of γ -methyl groups decrease from lignite through the high volatile bituminous coal range and then increase slightly in the Upper Freeport and Pocahontas extracts.

CONCLUSIONS

Comparing the ¹³C NMR data on the extracts and residues, it becomes apparent why material is extracted from the parent coal. While the CP/MAS spectra of both the extracts and residues are quite similar, an examination of the details of the structure provide the subtle differences in structural detail that are important in describing the extraction process. While one must recognize that we are observing the averages of all the components present in the extracts, the extracted material appears to have many of the structural features that are observed in the macromolecular structure of the coal. The

differences lie in the fact that the number of cross links is reduced and the number of substituents on the aromatic rings is lower in the extracts than in the residues. Hence, these data are consistent with the fact that this material can be extracted since it is not extensively incorporated by means of covalent bonds into the macromolecular structure. The proton NMR data shows that the amount of 2- and 3-ring components present in the extracts increases with the rank of the coal. The aliphatic region of the proton NMR data indicates that: a) the amount of α -methyl groups is essentially the same in all extracts, b) the amount of γ -methyl groups decreases with rank, and c) the amount of α -hydrogen goes through a maximum at the high volatile bituminous rank range.

These data on the extracts will be used to compare the pyridine extractable material that is obtained as these coals are pyrolyzed. Experiments that are now underway in our laboratories together with the results presented herein will be useful in our future work on modeling the transformation that occur during devolatilization and char formation.

ACKNOWLEDGMENT

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Table 1
Pyridine Extraction Yields

Coals	Extractable Yield (%)^a	Residue Yield (%)^a	Total Recovery
Stockton	13.8	80.2	94.0
	15.6	80.5	96.1
Pittsburgh #8	26.0	69.1	95.2
	27.0	70.5	97.5
Blind Canyon	31.1	65.3	96.4
	33.1	64.6	97.5
Illinois #6	27.3	67.3	94.6
	28.5	65.1	93.6
Upper Freeport	14.8	81.8	96.6
	15.0	82.7	97.7
Wyodak	6.1	92.4	98.5
	6.3	91.7	98.0
Zap	3.0	94.5	97.5
	3.2	94.7	97.9
Pocahontas	0.5	96.8	97.3
	0.5	97.2	97.7

^a Weight percent on a dry basis.

PROTONATED AROMATIC CARBONS IN PYRIDINE EXTRACTS AND RESIDUES FROM ARGONNE COALS

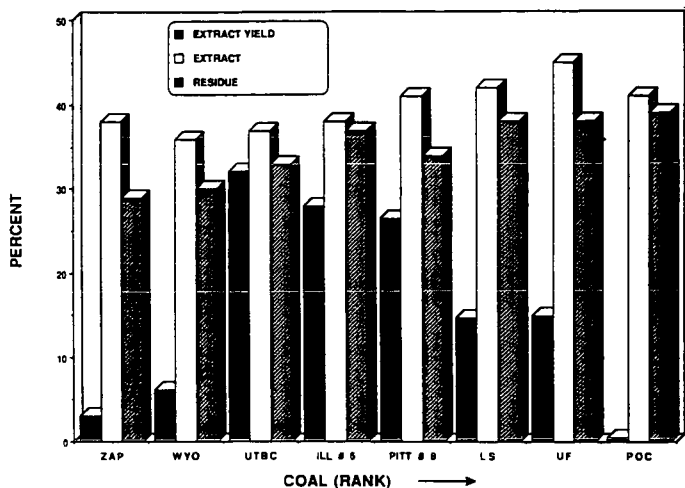


Figure 1. Extract yields and fraction of total aromatic carbons that are protonated (f_6H) in pyridine extracts and residues of the APCS coals.

COORDINATION NUMBER IN PYRIDINE EXTRACTS AND RESIDUES IN ARGONNE COALS

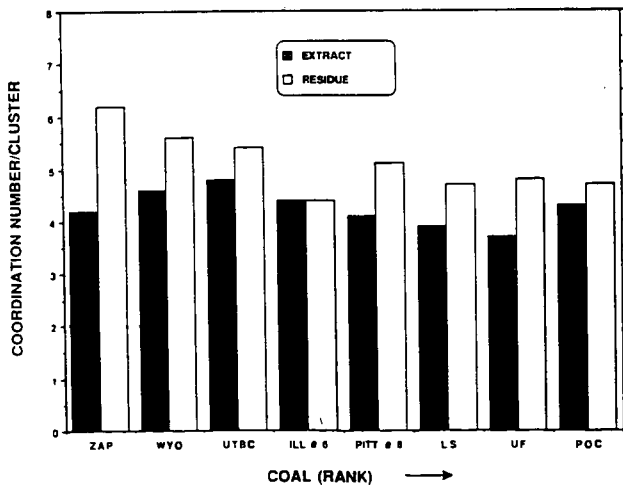


Figure 2. Coordination number in pyridine extracts and residues of the APCS coals.

BRIDGES AND LOOPS IN PYRIDINE EXTRACTS AND RESIDUES FROM ARGONNE COALS

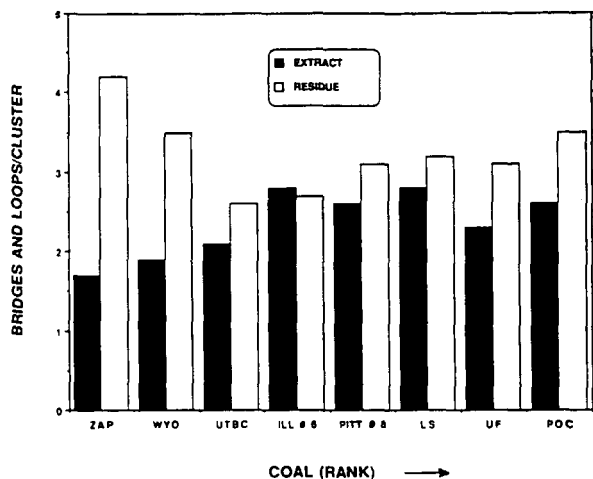


Figure 3. Number of bridges and loops per cluster in pyridine extracts and residues of the APCS coals.

AVERAGE AROMATIC CLUSTER SIZE IN PYRIDINE EXTRACTS AND RESIDUES FROM ARGONNE COALS

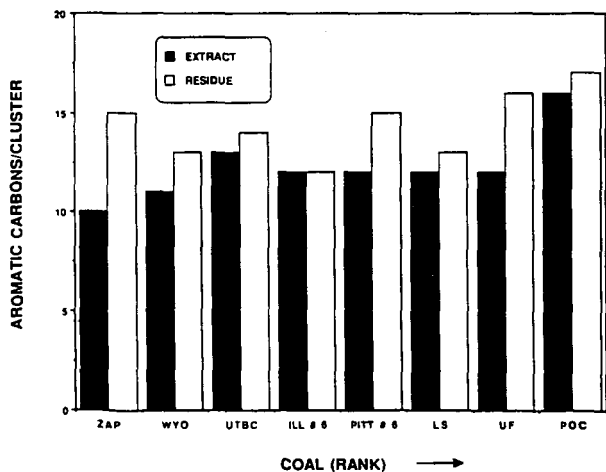


Figure 4. Average aromatic cluster size in the extracts and residues of the APCS coals.

SIDE CHAINS IN PYRIDINE EXTRACTS AND RESIDUES FROM ARGONNE COALS

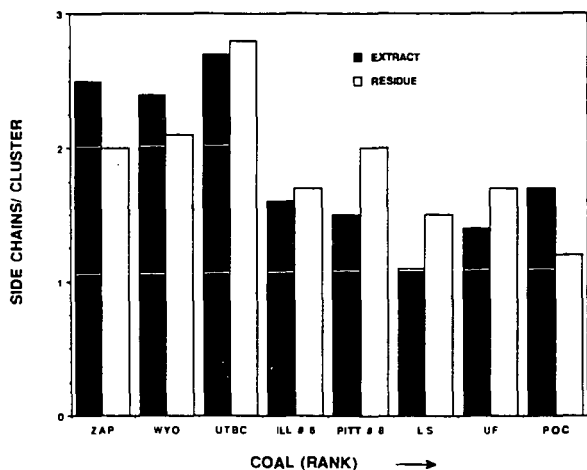


Figure 5. Number of side chains per cluster (coordination number) in the extracts and residues of the APCS coals.

AROMATIC CHARACTERISTICS OF PYRIDINE EXTRACTS FROM ARGONNE COALS

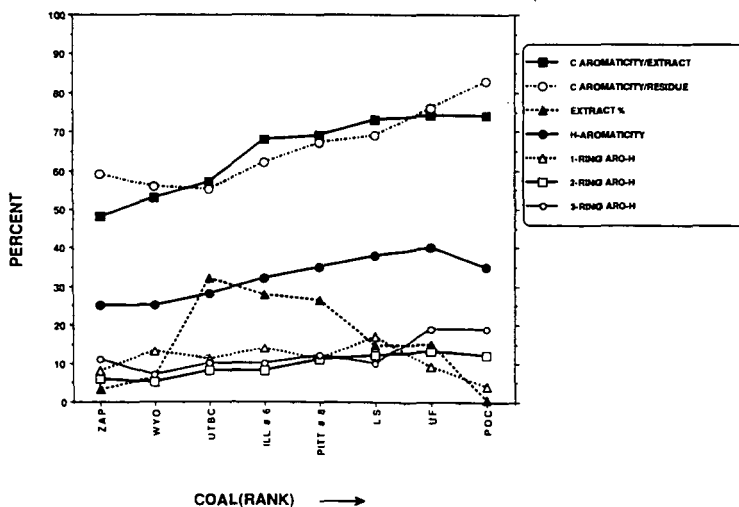


Figure 6. Aromatic characteristics in the extracts and residues of the APCS coals.

ALIPHATIC PROTON STRUCTURAL PARAMETERS IN PYRIDINE EXTRACTS FROM ARGONNE COALS

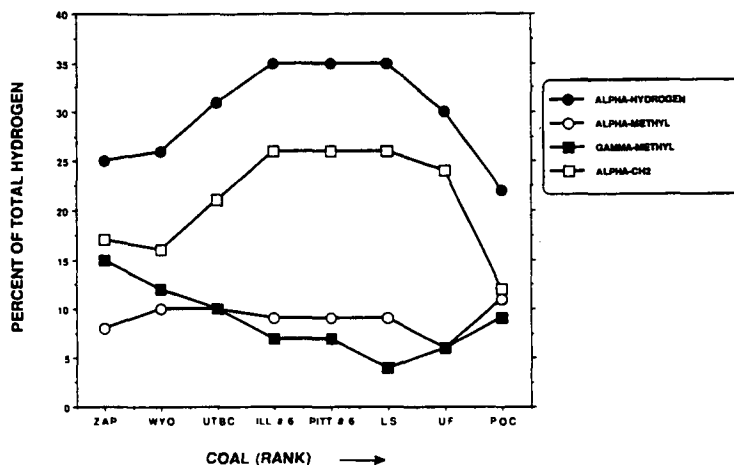


Figure 7. Aliphatic proton structural parameters of the APCS coals.